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Composite fiber with excellent dimensional stability, and its manufacturing method

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[1. TITLE]

Composite fiber with excellent dimensional stability and its manufacturing method

[2. claim]

(1)

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It is the fiber which compounds polyphenylene sulfide polymer layer (A) and protection polymer layer (B) consisting of a fiber-forming property thermoplastic polymer which are made to be main structural units. Dry heat shrinkage, of which the boiling-water coefficient of contraction of these composite fibers is 1.0 % or less at 80 degrees-Celsius, is 2.0 % or less.

Composite fiber with excellent dimensional stability characterized by the above-mentioned.

(2) Composite fiber with excellent dimensional stability of the claim 1st term description which is polyester with which a protection polymer layer has a polyethylene terephthalate or a polybutylene terephthalate as a main component.

(3)

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It treats a fiber, which makes this a main structural unit and is compounded polyphenylene-sulphide polymer layer (A) and protection polymer layer (B) consisting of a fiber-forming property thermoplastic polymer, by the oxidizing agent chosen from hydrogen peroxide, an alkali-metal hypochlorite, an alkaline-earth-metal hypochlorite, sulfuric acid, hydrochloric acid, sulfuryl chloride, nitrogen dioxide, chromium trioxide, alkali-metal permanganate, nitric acid, organic peroxy acid, lead tetraacetate, periodic acid, periodate, or N- halo carboxylic acid amido.

The manufacturing method of the composite fiber with excellent dimensional stability characterized by the above-mentioned.

[3. DETAILED DESCRIPTION OF INVENTION]

[INDUSTRIAL APPLICATION]

This invention relates to the composite fiber with excellent dimensional stability, and its manufacturing method.

[PRIOR ART]

As for dimensional stability of a woven fabric, knitted fabric, etc., what was latent as cloth raw material property and stress or heat-shrink power according to the past record received in the process by which they were manufactured, appears as a dimensional change in the conditions which are to carry out use or processing. It is the contraction at the spreading time in the sewing process, iron press contraction, wash contraction of real time-of-use, etc. that pose a problem.

Moreover, the finish before the sewing process, that is, even if it sets in processes, such as a thermosetting, refinement * coloring, and a fabric machine, it is important as process permeability and the dimensional stability of a fabric machine and the fiber itself from the surface of the texture after completion (it may be more appropriate to say that it is contractile in the case of the fiber).

In the case of natural fiber like the protein fiber or the cellulosic fiber, mainly a swelling of the direction of a fiber diameter by the water component, contraction of the cloth accompanied to this by contraction of fiber axial direction, and the contraction in the case of synthetic fiber, in cases such as when distortion received in the fiber-formation * drawing process of a thread does not relieve enough and an impossible spreading is performed, that of which stress and heat-shrink power remain in cloth receives the effect of heat and water components of the iron pressing step and it contracts.

Contraction which is cloth as mentioned above is determined by the amount which the shrinkage force of these fibers themselves and cloth may contract.

However, in order to make dimensional stability favorable, the subject which should 1stly be tackled is improvement of the heat-shrink of the fiber itself.

It is proper that the degree and application determine a knitted structure and a density.

The heat stability of the fiber and heat resistance are greatly influenced by the crystallinity.

The crystallization section of the molecular chain which constitutes the fiber is very rigid, and stable also to heat.

At an amorphous part, it is on the contrary.

a molecular chain is easy to move and unstable to heat.

Moreover, increasing the heat resistance is known for the field of synthetic fiber by transducing an aromatic ring into a molecule principal chain.

This is based on effects by aromatic-ring transduction, such as increase of the rigid property of a principal chain, and increase of C- H-coupling power.

Now, there is polyethylene-terephthalate (henceforth, PET) fiber to all occupy at least the most important ground as general-purpose fiber.

The PET fiber is excellent in the dyeability with a certain amount of heat stability which has that a melt spinning is made and a suitable elasticity * strength.

Since it has the many strong points of these, etc., the application is large regardless of the garments field, the interior field, and an industrial field.

This belongs to an aromatic polyester.

Although it is the crystalline fiber which has an aromatic ring in a principal chain, since the ratio of an aromatic ring is small, structure is hard to be called heat resistance.

An aromatic polyamide is known as heat-resistant fiber.

This is the fiber which Dupont industrialized for the first time in 1967.

However, since it is inferior to a dyeability and weatherproofing fastness, the applications, such as protection garments, and a laundry article, an electrical insulation material, are restricted.

Moreover, in order to improve a dyeability, the trial (Japanese Patent Publication No. 45-34766) which improves a sulfone group is also made.

However, an strength, a Young's modulus, thermal contraction rate, etc. were inferior compared with an average, and deviate from the inherent objective.

In addition, since this fiber manufactures by the wet-spinning method, its process is complicated and development of the application raw material is difficult.

In recent years, the melt spinning was possible and the polyphenylene sulfide polymer was developed as a polymer which has heat-resistant * flame retardance.

This polymer is rich in a crystallinity, and since the ratio of an aromatic ring is also high, that crystallization is very rigid and heat stability is high.

Moreover, since a melt spinning can be carried out, and manufacture by the polyester base under present operation can be performed basically, the anticipation as general purpose high-functional fiber substituting for the PET fiber will be great in the future.

However, because this polymer has the misfortune of high crystallinity, dyeability is bad, and also texture of the thread has a hard feeling, etc.

the property of a polyester fiber was not cleared in all respects.

As mentioned above, various heat-resistant fibers are developed and marketed today.

However, the evaluation is not perfect.

[PROBLEM ADDRESSED]

Therefore, a melt spinning is possible for this invention, and it is excellent in the dimensional stability with respect to heat, and a dyeability is also favorable.

and the composite fiber of cheap cost and its manufacturing method will be obtained.

[SOLUTION OF THE INVENTION]

These inventors,

{⊙-s}

The fiber which compounded polyphenylene sulfide polymer layer (A) and protection polymer layer (B) consisting of a fiber-forming property thermoplastic

polymer which make this main structural units is obtained, by processing by the oxidizing agent which mentions these composite fiber later, it has the dimensional stability which was excellent harnessing the basic physical property by the polyphenylene sulfide polymer, it is found out that the fiber cheap also in cost is obtained, this invention was attained.

The polyphenylene sulfide polymer as used in the field of this invention consists of at least 90-mol% or more p- phenylene sulfide unit of a structural unit.

Moreover, even if it is containing the copolymerization component at a ratio of 10 mol% or less, it does not interfere.

For example, it can be a high polymer by the cross-linking component based on a less than 1-mol% trichloro benzene monomer and the cross-linking component by oxidation reaction being included.

Moreover, if another example is shown, a phenylene group can also be made into the one part biphenylene group, a naphthalene group, etc. in the range shown upwards, what substituted one part of a sulphide group by the oxide, the sulfone group, etc. similarly is applicable in the range which does not deviate from the main point of this invention.

As a polymer for a protection polymer layer formation, polyester which has a polyethylene terephthalate or a polybutylene terephthalate as a main component is suitable.

For example, aliphatic dicarboxylic acid, such as aromatic dicarboxylic acid, such as a terephthal acid, an iso phthal acid, naphthalene 2,6- dicarboxylic acid, a phthal acid, (alpha), a (beta)- (4-carboxy phenoxy) ethane, a 4,4'- dicarboxy diphenyl, and 5-sodium sulfo isophthalic acid, or adipic acid, and a sebacic acid, or these ester and ethylene glycols, diethylene glycol, 1,4- butanediol, a neopentyl glycol, a cyclohexane -1,4- dimethanol, a polyethyleneglycol, it is the fiber-forming property polymer compounded from diol compounds, such as the polytetramethylene glycol.

80 mol% or more of a structural unit is polyester whose 90 mol% or more is a polyethylene-terephthalate unit or a polybutylene-terephthalate unit specifically. Moreover, in polyester, the a small amount of additive agent, the fluorescent whitening agent, the stabilizer, or the ultraviolet absorber may be included.

It is going to obtain the fiber which serves as the objective by composite of a polyphenylene sulfide polymer and the polyester polymer in this invention.

However, favorable dimensional stability could not be obtained only by carrying out composite fiber-formation drawing, but spinning or after carrying out a weaving; it was found out by processing by the oxidizing agent that dimensional stability improves greatly.

The oxidizing agent used for processing is chosen from the group of a hydrogen peroxide, an alkali-metal hypochlorite, an alkaline-earth-metal hypochlorite, a sulfuric acid, the hydrochloric acid, a sulfuryl chloride, a nitrogen dioxide, the chromium trioxide, the alkali-metal permanganate, nitric acid, organic peroxy acid, lead tetraacetate, the periodic acid, the periodate, or N-halo carboxylic acid amide.

Many materials exist which show oxidation other than above.

However, objective of the invention was considered.

Consequently, the above-mentioned material was chosen.

Next, the suitable prescription about each processing agent is shown.

It uses a hydrogen peroxide, an alkali-metal hypochlorite, or alkaline-earth-metal hypochlorites by the density of the range of from 1.0 weight% until saturated as aqueous solution.

It uses a sulfuric acid by the density of the range from 10 % to 90 % as aqueous solution.

It can use the hydrochloric acid by the density of the range from 1.0 weight% to the saturated solution as aqueous solution of chlorine.

It uses a sulfuryl chloride by the density of the range to 40 to 90 weight% as a halogenated-hydrocarbon solution.

A nitrogen dioxide uses gas as it is.

It can use the chromium trioxide by the density of the range from 1.0 weight% to the saturated solution as aqueous solution.

It can use the alkali-metal permanganate by the density of the range from 1.0 weight% to the saturated solution as aqueous solution.

It can use nitric acid by the density of the range to 20 to 80 weight% as aqueous solution.

It uses organic peroxy acid in the range to 1.0 weight% - 80 weight%, and it is sold at aqueous solution.

It can use lead tetraacetate to the 1.0 weight%-saturated concentration by using benzene and an acetic acid as a solvent.

It can use the periodic acid and periodate in the density range to the 1.0 weight%-saturated solution as aqueous solution.

It can use N-halo carboxylic acid amide in the density range to the 1.0 weight%-saturated solution by using anhydrous methanol, methanol, benzene-methanol, etc. as a solvent.

Processing agents especially preferable in the upper prescription are a hydrogen peroxide, sodium hypochlorite, lead tetraacetate, a sodium periodide, N-bromo acetamide, a N-bromosuccinimide, N-bromo phthalimide, 1-chloro benzotriazole, etc.

Next, the manufacturing method of the composite fiber of this invention is demonstrated.

The fiber-formation apparatus outline of this invention is shown in FIG. 1.

It is filled with a polyphenylene-sulphide polymer in number 1 and a polyester polymer in number 2 of two sets of melting extruders.

By the extruder, it accurately measures the polymer style by which fusion extrusion was carried out with a gear pump, respectively, and it is sent to a fiber-formation head.

The pack metal fitting with which the head was equipped compounds two sorts of polymer styles, and after that, it is sent out from a spinneret and fiber formation is carried out.

The composite form of a polyphenylene sulfide polymer and the polyester polymer is chosen by the capability as which this fiber is required.

For example, it is better for the polyester protective layer to come to a sheath side, as shown to FIG. 2 in the field of which sufficient dyeability is required.

From a dyeability, when chemical-resistance and heat resistance are required, it thinks that it is better to make a polyphenylene sulfide layer into a sheath side as shown in FIG. 3.

In the composite form of the fiber of this invention, balance with an oxidation treatment poses a problem.

By acting on polyphenylene sulfide, an oxidation treatment improves heat stability.

Objective of the invention can be attained.

Therefore, the polyphenylene sulfide polymer layer should be arranged at the sheath part.

In the case of a core part, an oxidation treatment becomes difficult, generally an improvement of heat stability is considered that it cannot measure.

However, as a result of the present inventors doing earnestly examination, arrangement of a polyphenylene-sulphide polymer layer is not concerned with a core part or sheath part but an oxidation treatment advances to the same extent, a difference was not seen in improvement of heat stability.

That is, when seeing from a viewpoint of the dimensional stability with respect to heat, especially the composite form of both polymers did not need to be particular, and this fact became clear for the first time by this invention.

A spinning velocity is carried out similarly to a common fiber at 1000 m/min - several hundred 1000 m/min or 3000 to 5000-m/min high-speed fiber formation performs, or either is possible.

That into which the cross-linking went by the polyphenylene sulfide polymer will be inferior to a thread forming property, and will carry out a cut thread immediately.

However, a non-bridge type polymer is excellent in the pulling thread very much, a composite with the polyester polymer is also favorable, remarkable high-speed fiber formation is also possible, and there is no exfoliation etc.

Drawing is possible in a normal roller plate mold drawing machine.

An Example is shown below; the content of invention is demonstrated in detail.

However, the boiling-water coefficient of contraction (W1) and dry heat shrinkage (W2) in this specification tell the value calculated with the following method.

$$W_1 = \frac{L_1 - L_2}{L_1} \times 100 (\%)$$

Sample length of the boiling-water before processing measured applying the load of 1:0.051/d, sample length after the boiling-water treatment measured applying the load of 2:0.05 g/d, treatment

inserted a sample (50 cm) in 98 degrees-Celsius boiling water and applied a load of 0.5 mg/d and treated it for 30 minutes.

$$W_2 = \frac{L_1 - L_2}{L_1} \times 100 (\%)$$

Sample length of the dry-heat before processing measured applying the load of 3:0.05 g/d, sample length after the dry-heat processing which measured applying the load of 14:0.05 g/d, processing adds a sample (50 cm) into 180 degrees-Celsius dry-heat air, the 0.51 mg/d load was applied and it processed for 10 minutes.

[Example 1]

The polyethylene terephthalate of $[(\eta)] = 0.80$ which added TiO_2 0.5 wt% is extruded with 40 (phi) extruder, on the other hand, polyphenyl sulfide with a viscosity of 4000 poises (300 degrees-Celsius 10sec) is extruded from 40 (phi) extruder with a non-bridge mold, after carrying out predetermined-amount measurement, respectively, it washes away in a fiber-formation pack, it sends out from a round-hole nozzle, composite fiber formation was performed by 1000 m/min of spinning velocities.

The cross section of a composite yarn is compounded so that it may come out like FIG. 3 (a), it may be and polyphenylene sulfide may occupy 20% of a total fiber surface area.

This fiber-formation base thread is drawn on a roller plate, the multifilament of 75-denier 24 filaments was obtained.

This drawing thread is made to be a diameter of about 12, a skein of about 3 cm. A phase etc. is made to available-chlorine density 3.0 g/l and pH is adjusted with the acetic acid to 4.0 by the weight of 50 times a thread sample, an injection, immersion is carried out into a sodium-hypochlorite solution, and oxidation treatment was performed at 80 degrees-Celsius for 60 minutes.

After that, it neutralizes, washes in water and dries, the boiling-water coefficient of contraction W1 and dry heat shrinkage W2 after processing were measured.

W1 is as extremely low as 0.5 %, W2 is as extremely low as 1.7 %.

It was found that these composite fibers are excellent in the dimensional stability with respect to heat.

Moreover, on the other hand, the knitted fabric was knitted with the drawing thread of these composite fibers, and the coloring test was tried.

Eastman polyester navy blue 3RLS is used for the stain.

it carried out at 2-% owf and a bath ratio 50:1, 130 degrees-Celsius for 1 hour.

It was 82 % when percentage exhaustion was measured.

It is thought that all the polyethylene-terephthalate polymers that it compounded from the percentage exhaustion of the polyethylene-terephthalate ground colored on these conditions as a control being 95 % are colored.

Since the polyphenylene sulfide polymer section exposed to the fiber surface 20% is difficult to color, its color is somewhat thin.

However, when seeing as a whole, level-dyeing property was favorable.

[Example 2]

The arrangement of the polymer in Example 1 is made reverse, others performed fiber formation, drawing, an oxidation treatment, W1, W2 measurement, and coloring on these conditions.

The result similar to Example 1 was almost obtained with W1=0.7% and W2=1.7%.

Percentage exhaustion was 65 %.

[Comparative Example 1]

W1 and W2 were measured without treating the same drawing thread which used in Example 1.

W1=5.0%, W2=13.0%, and heat shrink were quite large.

[Comparative Example 2]

W1 and W2 were measured without treating the drawing thread which used in Example 2.

It is showing that it is comparable as W1=6.5%, W2=13.0%, and Comparative Example 1, and is large, and dimensional stability is unsatisfactory.

[Example 3]

The polyethylene terephthalate of $[(\eta)] = 0.65$ which added TiO_2 0.5W% is extruded with 40 (phi) extruder, on the other hand, polyphenylene sulfide with a viscosity of 2000 poises (300 degrees-Celsius 10sec) is extruded with 40 (phi) extruder in a non-bridge mold, after carrying out predetermined-amount measurement, respectively, it washes away in a fiber-formation pack, it sends out from a round-hole nozzle, composite fiber formation was performed by 3600 m/min of spinning velocities.

The cross section of a composite yarn is a perfect core sheath which makes a sheath as a polyethylene terephthalate and makes a core polyphenylene sulfide like FIG. 1 (a).

The composite weight ratio of a polyethylene terephthalate and polyphenylene sulfide was 80:20.

It treated without drawing this fiber-formation base thread.

Processing was performed with the bath ratio 1:60 for 1 hour in anhydrous 81-% methanol solution 3 degrees-Celsius of a N-bromosuccinimide (NBS).

After treatment with methanol, water, by the method similar to Example 1 after cleaning, when the coefficient of contraction was measured, hot-water coefficient of contraction W1 is 0.6 %, dry heat shrinkage W2 is 1.8 %, and the heat stability which was excellent.

[4. Brief Description of Drawings]

FIG. 1 is a schematic diagram of the fiber-formation apparatus which obtains the composite fiber of this invention, FIG. 2 and FIG. 3 are a cross-sectional figure row which shows the composite form of the fiber of this invention.

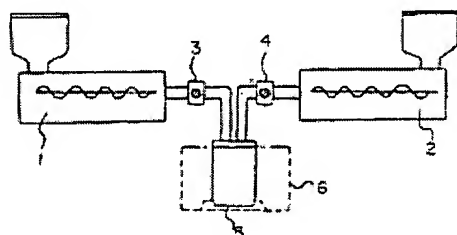
[PATENTEE]

Kuraray, K.K.

[REPRESENTATIVES]

Patent attorney Ken Honda

[FIG. 1]



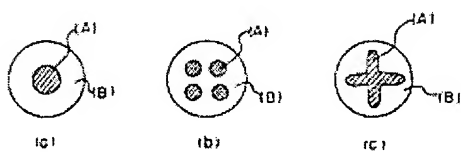
紡糸装置概略図

- 1. 溶融押出機 I
- 2. 溶融押出機 II
- 3. ギャーポンプ I
- 4. ギャーポンプ II
- 5. 紡糸口金
- 6. 紡糸ヘッド

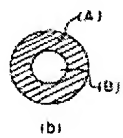
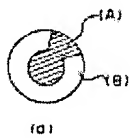
Fiber-formation apparatus schematic diagram

- 1. Melting extruder I
- 2. Melting extruder II
- 3. Gear pump I
- 4. Gear pump II
- 5. Spinneret
- 6. Fiber-formation head

[FIG. 2]



[FIG. 3]



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